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Zinc Acetate as a Catalyst for *Di*- and *Tri* imide Formation from 1,8-Naphthalic Anhydride and Aromatic Polyamides

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Six-membered naphthalic anhydrides are more stable and less reactive towards amine groups than their five membered ring counterparts.¹ There is a great range of reactivity for aromatic polyamides which depends on the spatial relationship between the various amine groups. For 1,4-diaminoarenes, imide formation at one amine can suppress reaction at the other amine.^{2,3} This effect makes it difficult to prepare six-membered aromatic diimides from 1,4-phenylenediamine. For example Hodgkin^{2b} reported that the condensation of 1,8-naphthalic anhydride (**4**) and 1,4-phenylenediamine (**3**) in DMSO or DMF at reflux give only *mono* imide while a 3 : 2 ratio of *mono* imide and *di* imide **1** was formed in DMAC at reflux for 24 hrs.

The condensation of bisanhydrides and aryl monoamine under $Zn(OAc)_2 \cdot 2H_2O$ catalysis has been used to prepare *mono* imides.⁴ In this study, we use zinc acetate dihydrate as a catalyst to form the naphthalic *di* imide **1** and naphthalic triimide **2** (Figure 1).

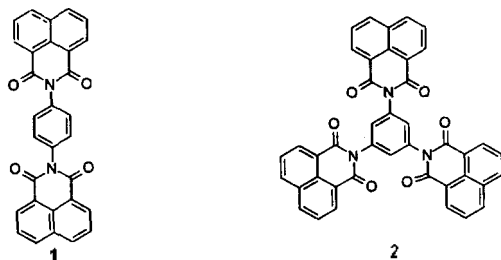
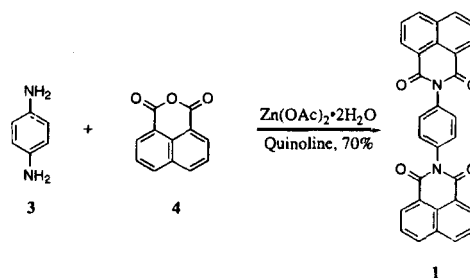


Figure 1. Naphthalic Diimide **1** and Naphthalic Triimide **2**.

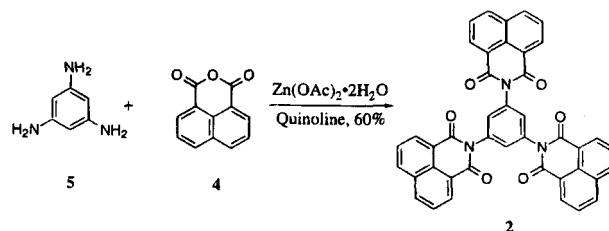
The six-membered aromatic *di* imide **1** was prepared from 1,4-phenylenediamine (**3**) and 1,8 naphthalic anhydride (**4**) in the presence of a catalytic amount (10 mol %) of $Zn(OAc)_2 \cdot 2H_2O$ in quinoline (a 0.03 M solution) at 200 °C. In this reaction the *di* imide **1** was formed in 70% yield uncontaminated by *mono* imide (Scheme 1).

Alternatively, the aromatic *tri* imide **2** was synthesized from 1,3,5-phenylenetriamine (**5**)⁵ and naphthalic anhydride (**4**) under similar conditions in 60% yield (Scheme 2).

In summary, we have shown that six-membered ring *di*-



Scheme 1.



Scheme 2.

imides and *tri* imides can be prepared using $Zn(OAc)_2 \cdot 2H_2O$ as a catalyst. We will apply this result to the preparation of polymeric versions of six-membered arylimides **1** and **2** from polyamine monomers **3** and **5**.

Experimental

General. All commercial chemicals were used as obtained without further purification, and all solvents were carefully dried and distilled by standard methods prior to use. Column chromatography was carried out on silica gel 600 (E. Merck, 230-400 mesh) with the flash technique.⁶ Nuclear magnetic resonance spectra were recorded on either WP-200 or AM-300 spectrometer. Chemical shifts are reported in δ ppm relative to $(CH_3)_4Si$ for ¹H NMR. Coupling constants, *J*, are reported in Hz. Infrared spectra (cm^{-1}) were obtained on a Perkin-Elmer 1600 FT infrared spectrometer. Positive fast atom bombardment mass spectra

(FABMS) were obtained in a 2-nitrophenylether matrix. Combustion analyses were performed by Midwest Micro-labs, Indianapolis, IN.

Naphthalic di imide 1. The mixture of 1,8-naphthalic anhydride (**4**) (1.59 g, 8.03 mmol), 1,4-phenylenediamine (**3**) (0.43 g, 4.02 mmol), and Zn(OAc)₂ · 2H₂O (0.09 g, 0.41 mmol) was dissolved in 10 mL of quinoline. The solution was stirred in 120 °C for 2 hrs, and then cooled to room temperature to get insoluble solid. The insoluble solid was washed with ethyl acetate (3 × 100 mL), H₂O (50 mL), and 1 M HCl (30 mL) to eliminate quinoline and then 1.32 g of the pure naphthalic di imide **1** as gray solid (70%) was obtained. IR (KBr) cm⁻¹ 1709, 1680; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (s, 4H), 7.82 (dd, *J*=7.23, 8.30, 4H), 8.30 (dd, *J*=1.04, 8.30, 4H), 8.70 (dd, *J*=1.04, 7.23, 4H); MS (FAB⁺) *m/z* 469 (M+1); Anal. Calcd for C₂₀H₁₆N₂O₄: C, 76.92; H, 3.44; Found: C, 76.86; H, 3.46.

Naphthalic tri imide 2. The mixture of 1,8-naphthalic anhydride (**4**) (0.3 g, 1.52 mmol), 1,3,5-phenylenetriamine (**5**) (0.06 g, 0.49 mmol), and Zn(OAc)₂ · 2H₂O (0.01 g, 0.05 mmol) was dissolved in 7 mL of quinoline. The solution was stirred in 120 °C for 2 hrs, and then cooled to room temperature to get insoluble solid. The insoluble solid was washed with ethyl acetate (3 × 50 mL), H₂O (30 mL), and 1 M HCl (30 mL) to eliminate quinoline and then 0.19 g of the naphthalic tri imide **2** as a light yellow solid (60%) was obtained. IR (KBr) cm⁻¹ 1709, 1672; ¹H NMR (300 MHz, CDCl₃) δ 6.75 (s, 3H), 7.78 (dd, *J*=7.39, 7.62, 6H), 8.24 (d,

J=7.62, 6H), 8.66 (d, *J*=7.39, 6H); MS (FAB⁺) *m/z* 664 (M+1).

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S-Acyl Derivatives of Benzothiazole-2-thiol: A Convenient Method for the Synthesis of Amides and Carbamates

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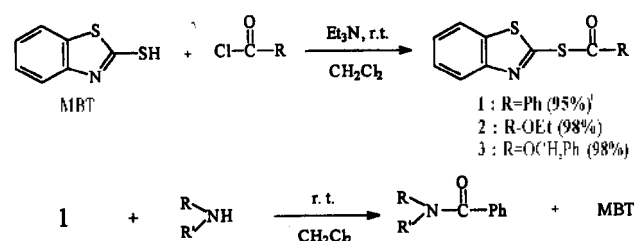
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In previous papers,^{1,2} many useful acylating reagents have been extensively exploited for the synthesis of amides. In connection with our research directed toward synthetic utility of active S-esters and S-carbonates containing benzothiazole-2-thiol moiety, the so-called 2-mercaptobenzothiazole (MBT) in the rubber industry, we wish to report the use of a new class of improved acylating reagent, S-acyl derivatives of MBT for the synthesis of amides and carbamates.

S-Acyl derivatives of MBT were easily prepared by mixing equimolar amounts of benzoylchloride or alkyl chloroformate, MBT, and triethylamine in dichloromethane at room temperature in quantitative yields.

The reaction of S-benzoyl-2-benzothiazole thioester (**1**) as a model compound with several amines was carried out. The thioester (**1**) easily reacted with primary amines and secondary amines to give quantitative yields of the corresponding amides within 5 min. in dichloromethane at room temperature (Scheme 1). On the other hand, benzoyl-

ation of aniline and tertiary butylamine was carried out in benzene under reflux. The thiolate moiety of MBT having the excellent leaving property was easily removed by washing the reaction mixture with dil. alkaline aqueous solution, and the solvent was evaporated off in vacuo to afford only desirable amides in quantitative yields without further purification (Table 1). In particular, aminoalcohols, for ex-



Scheme 1.